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A PRELIMINARY NOTE ON THE DECOMPOSITION OF CALCIUM CYANAMIDE IN SOUTH INDIAN SOILS

STORAGE

BY

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A PRELIMINARY NOTE ON THE DECOMPOSITION OF CALCIUM CYANAMIDE IN SOUTH INDIAN SOILS.*

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[Received for publication on 6th February, 1923.]

CALCIUM CYANAMIDE or nitrolim is a nitrogenous fertilizer containing about 20 per cent. of nitrogen derived from the atmosphere.

In Europe, where great developments have taken place in its manufacture, this manure is in common use and has given results very little inferior to ammonium sulphate.

In South India, on the other hand, where a number of trials have been carried out in recent years, the results have been disappointingly erratic. In view of the probable development of hydro-electric power schemes in this country which should render possible the manufacture of the fertilizer at a reasonable cost, it has seemed desirable to re-examine the whole question both in the laboratory and by means of field trials. The work is still very incomplete, but some of the preliminary results obtained may be described with advantage.

Meantime we are continuing the investigation paying particular attention to the factors controlling the formation and decomposition of dicyanodiamide and the differential action of the latter on the nitrification of organic manures as opposed to mineral manures of which we have obtained some evidence. The residual effects, if any, of cyanamide will also be examined.

* Paper read before the Indian Science Congress, January 1923.

Balakrishnamurthi[1] has summarized the results of field trials on the various Government Farms in Madras between the years 1916 and 1920. This summary clearly shows the erratic nature of the results. In some cases the manured plots gave yields lower than the controls, while in others, where an increase was shown, this was so small as to be within the experimental error, or at any rate insufficient to cover the cost of the manure. Many of these experiments, however, were unsatisfactory having been carried out in single or duplicate plots only and hence, as Balakrishnamurthi points out, the results cannot be very seriously entertained.

Field trials.

1919-1920 *and* 1921-1922. The results of experiments conducted on the Central Farm, Coimbatore, during the years 1919-1920 and 1921-1922 with *tenai* (*Setaria italica*), *ragi* (*Eleusine coracana*) and paddy (*Oryza sativa*) on red, garden and wet lands respectively are given in Tables I to IV.

Table I.

Dry red soil. Crop *tenai* (*Setaria italica*).

	No. of plot	Area in cents	Yield in pounds	Acre yield in pounds
Manured	1	5	38	760
	3	5	42	840
	5	5	46	920
	7	5	46	920
	9	5	38	760
Total ..	..	..	210	4,200
Unmanured . ..	2	5	36	720
	4	5	28	560
	6	5	36	720
	8	5	37	740
	10	5	38	760
Total ..	..	..	175	3,500

Average .. Manured		840
Unmanured		700
	..	per cent.
Percentage increase		20
Probable error of individual plots		± 9·10
Probable error comparing two sets of five plots each		± 5·74

[1] Balakrishnamurthi. *Year Book, Dept. of Agri., Madras*, 1920-21.

This field was prepared in August, and 10 five-cent experimental plots (300 links$\times 16\frac{2}{3}$ links) were laid out across the field. Nitrolim was applied to alternate plots at the rate of 1 cwt. per acre on 4th August, 1919, and was worked into the soil by the Junior hoe. After the application of the manure a drought intervened so that the sowing of seed was delayed until 15th September, 1919. The germination in all plots was satisfactory, but from the beginning the manured plots showed the more vigorous growth and this continued till harvest time. The amount of rainfall received for the crops was 15·29 inches and this was fairly distributed throughout the period the crop was on the land.

TABLE II.

Red soil. Irrigated *ragi* (*Eleusine coracana*).

	No. of plot	Area in cents	Yield in pounds	Acre yield in pounds
Manured	1	5	123	2,460
	3	5	148	2,960
	5	5	152	3,040
	7	5	144	2,880
	9	5	141	2,820
TOTAL		..	708	14,160
Unmanured	2	5	132	2,640
	4	5	133	2,660
	6	5	143	2,860
	8	5	130	2,600
	10	5	144	2,880
TOTAL ..	..	..	682	13,640

Average yield	Manured	2,832
	Unmanured	2,728
		per cent.
Percentage increase		3·80
Probable error of individual plots		± 4·36
Probable error comparing two sets of five plots each ..		± 2·75

The preliminary cultivation was completed on 21st June, 1919, and 10 five-cent experimental plots (400 links $\times 12\frac{1}{2}$ links) were prepared. The experimental plots were laid out in beds and the manures applied to alternate plots at the rate of 1 cwt. per acre on 23rd June, 1919. Irrigation was given and the *ragi* (seedlings) plants which had previously been raised in a nursery in F. No. 19 were planted in puddle on the 29th June, 1919. The crop received two hoeings and 8 irrigations in addition to rainfall of 4·8 inches. The crop grew well throughout but except that the manured plots remained a darker green there was no other visual difference.

TABLE III.

Wet land. Paddy (*Oryza sativa*). 1919-1920.

	No. of plot	Area in cents	Yield in pounds	Acre yield in pounds
Manured	1	5	231	4,620
	3	5	224	4,480
	5	5	224	4,480
	7	5	224	4,480
	9	5	258	5,160
TOTAL ..	..	..	1,161	23,220
Unmanured	2	5	200	4,000
	4	5	212	4,240
	6	5	206	4,120
	8	5	163	3,260
	10	5	164	3,280
TOTAL ..	..	..	945	18,900

Average	Manured	4,644
	Unmanured	3,780
		per cent.
Percentage increase		22·70
Probable error of individual plots		± 9·36
Probable error comparing two sets of five plots each		± 5·90

Puddling operations were completed on 2nd September, 1919, thereafter 10 five-cent plots were laid out and nitrolim applied to alternate plots at the rate of 1 cwt. per acre. Transplanting commenced on 4th September, 1919, with seedlings taken from the nursery in C Block. The seedlings at the time of planting were especially good, being robust and vigorous. All plots grew very well and a slight difference was noticed in favour of the manured plots. The season was a particularly favourable one for paddy and the crop which was harvested on 30th December, 1919, yielded as shown below :—

TABLE IV.

Wet land. Paddy (*Oryza sativa*). 1921-1922.

	No. of plot	Area in cents	YIELD PER PLOT IN LB.		YIELD PER ACRE IN LB.	
			Grain	Straw	Grain	Straw
Unmanured ..	1	5	155	196	3,100	3,920
	3	5	134	200	2,680	4,000
	5	5	156	236	3,120	4,720
	7	5	140	168	2,800	3,360
Manured	2	5	164	224	3,280	4,480
	4	5	138	228	2,760	4,560
	6	5	146	144	2,920	2,880
	8	5	134	148	2,680	2,960
Average for unmanured ..	..	..	146	200	2,925	4,000
Average for manured	..	..	145	186	2,910	3,720

These results are again as erratic as those summarized by Balakrishnamurthi. They have, however, not been so unfavourable as those independently conducted by the Superintendent, Central Farm, Coimbatore, during the previous year when the unmanured plots gave higher yields than the calcium cyanamide plots. The figures of 1919-1920 showed varied increases in favour of nitrolim, and while they were not sufficiently high, except in the case of

paddy, to claim any definite result in favour of the manure, it was considered that the case was sufficiently interesting to warrant further investigation.

In one or two cases the failure of the manure to bring about any marked increase of crop may be attributed to the fact that the experiments were conducted on land already containing a fairly high percentage of nitrogen, while in others a deficiency of phosphoric acid may have been a limiting cause. It is obvious, of course, that these two factors demand careful consideration in laying down plots for any manurial experiment.

In those cases where the application of nitrolim has definitely depressed the yield, this effect has usually been attributed to the formation of dicyanodiamide, a substance believed to have toxic powers.

It was obviously desirable to deal with this latter point first and to ascertain, if possible, the fate of nitrolim in the soil under the conditions prevailing in this country.

A considerable amount of work has been done in Europe and America since nitrolim was first put on the market. Aso[1], Loew[2], Ulpiani[3], Kappen[4], Brioux[5] and Russell[6] are among the earliest investigators who paid considerable attention to the subject, while later contributions have been made by Cowie[7] of the Rothamsted Experiment Station. Cowie gives a brief summary of the earlier work and the results of his own investigations in regard to the decomposition of calcium cyanamide in the Rothamsted and Woburn soils.

Cowie's conclusions were as follows :—

1. Cyanamide readily breaks down in the soil yielding ammonia, which then nitrifies in the usual way. The conversion of cyanamide nitrogen into nitrate is practically quantitative and its effectiveness as a fertilizer is approximately equal to that of ammonium sulphate.

2. Dicyanodiamide has given no evidence of nitrification in the soil even after several months. On the contrary, it is actually toxic to plants, although

[1] Aso. *Jour. College Agri.*, Tokyo, **1**, 1909—1913, 193.
[2] Loew. *Chem. Zeit.*, 1908, No. 57 ; 1909, No. 3.
[3] Ulpiani. *Cent. für. Bakt.* Abt. II, Bd. **18**, 1907, 55.
[4] Kappen. *Cent. für. Bakt.* Abt. II, Bd. **22**, 1909.
[5] Brioux. *Annales de la Science Agronomique*, III, Série 5, Année 1910, Tome I, 280.
[6] Russell. *Jour. Agri. Sci.*, VI, 53.
[7] Cowie. *Jour. Agri. Sci.*, IX, 113.

in small amounts it causes no appreciable injury. It does not affect germination at any of the concentrations used.

3. Dicyanodiamide is also toxic to the nitrifying organisms and stops the normal oxidation of ammonia in soils containing ammonium sulphate. It likewise inhibits the transformation into nitrate of the ammonia produced from cyanamide in the soil and causes an accumulation of ammonia under these conditions. It does not sensibly retard the formation of ammonia from cyanamide.

4. Dicyanodiamide does not appear to affect so drastically the other organisms of the soil, especially those concerned in the decomposition of protein. It exerts little influence upon the numbers developing on gelatine plate or the rate and extent of the decomposition of dried blood.

It will thus be seen that Cowie's work refers largely to the ammonification and nitrification of cyanamide in the soil and the influence of dicyanodiamide on these processes. He has not produced definite evidence in regard to the formation of dicyanodiamide in the soil, but conducted his experiments with dicyanodiamide prepared in the laboratory on the assumption that this was produced in the soil. It is of importance to ascertain whether this assumption is justified and if it be correct that dicyanodiamide is produced, to discover, if possible, the conditions which lead to its formation. Moreover, it seemed unjustifiable to assume that the decomposition of nitrolim in the soil, which can obviously take different courses, would necessarily be the same under the conditions prevailing in South India as was found to be the case in English soils. The difference in quality and texture of the soils, in agricultural practices, in climate and in soil temperatures between the soils of the two countries are so great that, in the absence of any information in regard to the decomposition of nitrolim in Indian soils, we considered it advisable to undertake a re-examination of the subject from the point of view of South Indian agriculture.

The general impressions prevalant in South India in regard to the use of calcium cyanamide are :—

1. That a certain interval of time is necessary between the application of manure and sowing.
2. The crop is liable to suffer owing to the formation of some toxic substance (dicyanodiamide) in the soil.
3. The nitrogen becomes available somewhat suddenly at a time when the crop is not able to utilize it to the greatest advantage.

In order to obtain definite information on the above points, the scope of enquiry, in its early stages, was limited to the following :—

1. What interval, if any, is necessary between the application of the manure and sowing or transplanting ?
2. What is the nature of the decomposition of calcium cyanamide in the soil ?
3. What are the products of decomposition and how quickly are these formed ?
4. Is dicyanodiamide formed at all in the soil, and, if formed, what is its ultimate fate ? Is it injurious and if so how ?

Interval between sowing and the application of manure.

Pot experiments and field trials were instituted to ascertain if any interval is necessary between manuring and sowing. In field No. 44 (Central Farm) a series of five-cent plots were laid out. In each series one plot was left unmanured as control and to four other plots calcium cyanamide at the rate of 1 cwt. per acre (20 lb. N per acre) was applied 3 weeks, 2 weeks, 1 week and 1 day previous to transplanting *ragi* (*Eleusine coracana*). There were thus 5 plots in each group and four groups or 20 plots in all. With the soil from the same field pot culture experiments on similar lines were started, the amount of nitrogen in this case, however, being about $2\frac{1}{2}$ times the amount used in the field. The results of these pot experiments and field trials are given in Tables V and VI and also shown photographically in Plate I, figs. 1–3. Similar pot experiments with paddy were also conducted, the results being given in Table VII.

Fig. 1. No manure. Manured 1 day before planting.

Fig. 2. Manured 3 weeks before planting. Manured 2 weeks before planting.

Fig. 3. Manured 1 week before planting. Manured 1 day before planting.

Fig. 4. Large doses of dicyanodiamide applied six months previously.

PLATE I.

POT EXPERIMENTS WITH RAGI.

TABLE V.

(Garden lands. Irrigated *ragi*.)

Showing yields of ragi (grain and straw). 1 cwt. nitrolim per acre applied at different times.

No. of series	No manure				Manure applied 3 weeks before planting				Manure applied 2 weeks before planting				Manure applied 1 week before planting				Manure applied a day before planting			
	Per plot		Per acre		Per plot		Per acre		Per plot		Per acre		Per plot		Per acre		Per plot		Per acre	
	Grain	Straw	Grain	Straw	Grain	Straw	Grain	Straw	Grain	Straw	Grain	Straw	Grain	Straw	Grain	Straw	Grain	Straw	Grain	Straw
	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.	lb.
1 ..	101	184	2,037	3,680	99	197	1,988	3,840	103	175	2,066	3,500	104	198	2,089	3,960	105	207	2,102	4,140
2 ..	114	204	2,286	4,080	115	217	2,306	4 340	106	204	2,139	4,080	115	205	2,317	4,100	119¾	224	2,395	4,480
3 ..	115	211	2,307	4,220	116	224	2,333	4,480	105	205	2.115	4,100	112	219	2 244	4,380	112½	220	2,250	4,400
4 ..	114	202	2,282	4,040	116	204	2,321	4,080	120	216	2,409	4.320	117	208	2,354	4,160	107	179	2.146	3,580
TOTAL ..	444	801	8,912	16,020	446	842	8,948	16,740	434	800	8,729	16,000	448	830	9,004	16,600	444	830	8.893	16,600
AVERAGE ..	111	200	2,228	4.005	111½	210½	2,237	4,185	109	200	2,182	4.000	112	207½	2.251	4.150	111	207½	2.223	4,150

Averages.

	Per plot		Per acre	
	Grain	Straw	Grain	Straw
No manure	111	200	2,228	4,005
3 weeks before planting ..	111½	210½	2,237	4,185
2 weeks before planting ..	109	200	2,182	4.000
1 week „ ..	112	207½	2,251	4,150
1 day „ ..	111	207½	2,223	4,150

TABLE VI.

Showing results of pot experiments with ragi (*Eleusine coracana*), 1921.

(Manure applied at 100 milligrammes cyanamide N per kilogramme of soil.)

No. of series	Particulars of manure	Yield	
		Grain	Straw
		Grm.	Grm.
I	No manure	6·45	15·35
II	Manure applied 3 weeks before planting	16·57	31·98
III	„ „ 2 „ „ „	14·00	28·25
IV	„ „ 1 week „ „	13·07	21·58
V	„ „ 1 day „ „	16·07	30·98

TABLE VII.

Showing results of pot experiments with paddy (*Oryza sativa*), 1921.

(Manure applied at 100 milligrammes cyanamide N per kilogramme of soil.)

No. of series	Particulars of manure	Yield	
		Grain	Straw
		Grm.	Grm.
I	No manure	38·0	50·0
II	Manure applied 1 week before transplanting and immediately puddled	79·0	105·0
III	Manure applied 1 week before transplanting but not immediately puddled	93·0	110·0
IV	Manure applied a day before transplanting ..	76·0	111·0

The results clearly indicate that in these experiments the interval between manuring and transplanting had no influence on the resulting crop. In the field trials "no manure" plots have given the same results as the manured ones, while in pot experiments, on the other hand, the yield in the case of manured plots is nearly three times that obtained from controls. It was particularly

unfortunate that the land on which the field trials had to be made already contained a somewhat high percentage of nitrogen (0·12 per cent.). The amount of nitrogen added (20 lb. per acre) under these circumstances was perhaps hardly felt. In the case of the pot experiments where the application of nitrogen was much heavier, the results were much more favourable.

In this instance, however, it is sufficient to observe that no harmful influence of any sort was produced even when the interval between the application of the manure and transplanting was reduced to a minimum, either in field or in pot culture.

Decomposition of nitrolim in the soil.

When it is sought to follow the course of decomposition in the soil, serious difficulties are at once encountered. The existing methods of estimation of the substance likely to be produced are in several cases lacking in accuracy, especially in the presence of the other decomposition products. The methods of analysis have, therefore, had to be tested and standardized to suit our conditions. As a preliminary step it was decided to follow the course of decomposition determining (1) dicyanodiamide, (2) urea, (3) ammonia, (4) nitrite and (5) nitrate.

After numerous trials, urea, ammonia, nitrites and nitrates were determined by the methods employed by Cowie, with the exception that in determining urea the urease of red gram (*Cajanus indicus*) was used instead of soya bean urease which is not easily available in South India. Preliminary experiments had shown that *Cajanus* urease[1] was equally specific in action and gave results as satisfactory as those obtained with soya bean urease.

Dicyanodiamide is usually determined by Caro's method as modified by Brioux. This method consists in precipitating a solution containing calcium cyanamide and its decomposition products with silver nitrate in presence of caustic potash, collecting the precipitate and determining the nitrogen by Kjeldahl method. Both in the original Caro and the modified Brioux method, however, about 25 per cent. of the urea present is also precipitated along with the dicyanodiamide.

Harger[2] proposed a new method which depends on the fact that when a solution of silver picrate is added to a solution of dicyanodiamide, the latter is quantitatively precipitated as a double compound of silver picrate and dicyanodiamide. Neither cyanamide nor urea gives any precipitate when their solutions are treated with silver picrate, nor does their presence interfere with the

[1] Viswanath. *Agri. Jour. India*, Special Indian Science Congress Number, 1917.
[2] Harger. *Jour. Indus. Engineering Chem.*, **12**, 1107.

precipitation of dicyanodiamide. This method is certainly a great advance over the older one and generally gave satisfactory results in our preliminary tests. It had, however, to be standardized particularly in reference to the concentration of the dicyanodiamide in solution and also to the acidity of the solution.

The nature of the decomposition of cyanamide in the soil.

Two series of flasks were prepared each containing 100 grammes samples of soil, the moisture content of which being the same, *viz.*, 15 per cent. In the first series 0·06 gramme of nitrolim equivalent to 10 milligrammes nitrogen was added to each flask.

The second series was sterilized by autoclaving the flasks for 30 minutes at a temperature of 125°C., and to each flask was then added 0·06 gramme of nitrolim previously sterilized in a small tube.

The two series were, therefore, comparable except that the first contained the ordinary soil organisms while the second was sterile. The flasks, plugged with cotton wool, were then kept at room temperature and analyses made at intervals to ascertain the form in which the nitrogen was present. In this experiment nitrites and nitrates were not estimated, the decomposition being followed to ammonia stage only.

Later experiments indicate that sterilizing the soil at a high temperature may modify the behaviour of the latter. A better comparison would therefore be to sterilize both series and re-inoculate one.

Table VIII.

Showing the degradation of cyanamide in sterilized and unsterilized soils.

(10 milligrammes cyanamide nitrogen per 100 grammes of soil.)

Nitrogen as	Sterilized soil			Unsterilized soil		
	40 hrs.	4 days	7 days	40 hrs.	4 days	7 days
	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.
Cyanamide ..	23·0	4·0	0·00	1·1	0·00	0·00
Dicyanodiamide ..	0·0	0·0	0·00	0·0	0·00	0·00
Urea	Not determined		100·00	Not determined		3·73
Ammonia ..	Do.	Do.	0·00	Do.	Do.	6·17

In the case of sterilized soil no ammonia could be found even after 15 days.

In a second experiment the method of sterilizing the soil and manure, etc., was the same as before but the amount of cyanamide added was increased, being equivalent to 83 milligrammes N per 100 grammes of soil, a little over 8 times the amount used in the first experiment. The samples were analysed at the end of 14 days.

TABLE IX.

Showing milligrammes of nitrogen found in various forms after 14 days.

(83 milligrammes of cyanamide N per 100 grammes of soil.)

	Sterilized soil	Unsterilized soil
As Cyanamide ..	2·5	0·055
„ Dicyanodiamide ..	23·0	11·500
„ Urea	45·0	6·300
„ Ammonia	0·0	34·700

These results indicate that the decomposition of cyanamide in the soil under investigation is of a purely chemical nature up to the urea stage and that the hydrolysis of urea and the subsequent oxidation of the resulting ammonia are of a biochemical nature, thus confirming the observations of Ulpiani[1] and Cowie. The fact that the velocity of degradation in the soil sterilized at 125°C. is slower than that in the unsterilized soil and that it is slower still when the soil is ignited suggests that the transformation is one of physico-chemical nature. It will be noticed that in the first experiment when the concentration of nitrolim was normal there was no evidence of the ormation of dicyanodiamide. In the second case when high concentrations of nitrolim were employed considerable quantities were produced.

[1] Ulpiani. *Gazetta Chemica Italica*, **40**, 1910, 613, 666.

THE NATURE AND RATE OF FORMATION OF THE DECOMPOSITION PRODUCTS.

A detailed study of the nature and quantities of the products formed and of the rate of decomposition was next made with garden and paddy soils which analysed as follows :—

	Garden soil F. No. 44	Paddy soil, Wetland Block A.
	Per cent.	Per cent.
Moisture	3·54	3·63
Loss on ignition	5·01	4·95
Insolubles	73·05	72·87
Iron oxide	3·93	5·19
Alumina	6·99	9·79
Lime	2·12	0·97
Magnesia	1·40	1·42
Total phosphoric acid ..	0·05	0·07
Total potash	0·62	0·48
Undetermined	3·29	0·63
TOTAL ..	100·00	100·00
Nitrogen	0·123	0·043
Available phosphoric acid ..	0·028	0·010
Available potash	0·024	0·011
Fine gravel	9·17	3·55
Coarse sand	27·26	20·09
Fine sand	13·93	27·77
Silt	10·63	11·52
Fine silt	23·63	26·04
Clay	11·22	7·26
Water Extract		
Lime	0·009	0·006
Magnesia	..	..
Sulphuric acid	0·019	0·010
Carbonic acid	0·020	0·018
Chlorine	0·029	0·007
Total solids	0·150	0·064

4,500 grammes of the garden soil were passed through a 2 mm. sieve of round holes and mixed with small quantities of water at a time so as to bring the moisture content to 20 per cent. of the soil. Into this 2·70 grammes of calcium cyanamide were thoroughly incorporated. The mixture contained 100 milligrammes of cyanamide nitrogen per kilogramme of soil. That the manure was properly incorporated into the soil was ascertained by taking a sample and determining its nitrogen content by the Kjeldahl-Gunning method. The mixture was put into a series of small pots and analysed at intervals.

In the case of the paddy soil small quantities of the mixture of soil and manure were put into small beakers. Water was added until the soil was submerged and the contents were then puddled.

The results obtained are given in Tables X and XI and plotted in Chart I.

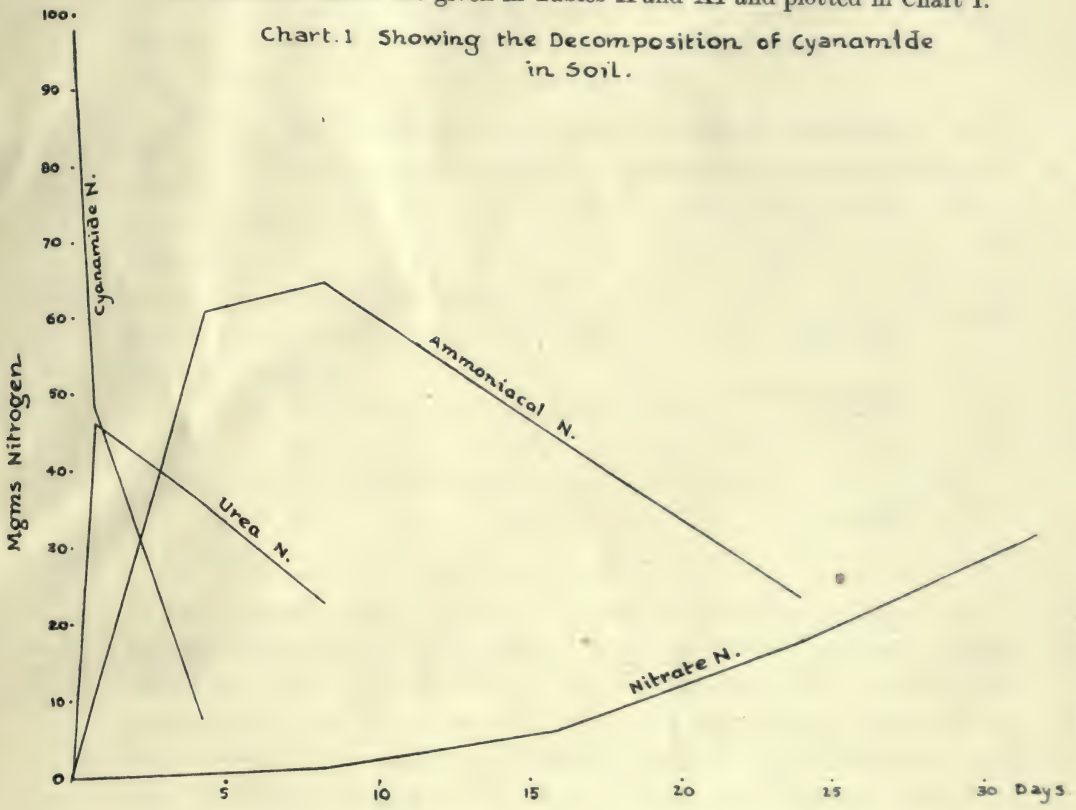

TABLE X.

Showing the decomposition of calcium cyanamide in the soil.

Garden soil F. No. 44.

(Cyanamide nitrogen 100 mg. per kilo of soil.)

	Initial	After 1 day	After 4 days	After 8 days	After 18 days	After 24 days	After 32 days
Cyanamide N ..	98·0	48·340	8·00	..	..	..	..
Dicyanodiamide N ..	..	..	..	..	..	..	..
Urea N	..	46·200	35·69	23·000	..	..	..
Ammonia N ..	..	..	60·82	65·000	..	24·30	..
Nitrite N	..	0·055	0·06	0·062	..	..	..
Nitrate N	..	..	..	1·300	6·37	18·22	32·0

TABLE XI.

Showing the decomposition of calcium cyanamide under puddled conditions.

(100 milligrammes of cyanamide N per kilo of soil.)

	After 2 days	After 25 days
Cyanamide N ..	6·30	....
Dicyanodiamide N ..	....	....
Urea N	16·80	8·40
Ammonia N	21·00	27·30

One striking feature of the results is that no dicyanodiamide can be detected when the quantity of manure applied is in consonance with agricultural practice. The results generally agree with those of Cowie. The decomposition of cyanamide in the soil is very rapid up to the urea and ammonia stages, the oxidation of ammonia to nitrates proceeding more slowly. Since nitrification proceeds at this slow rate there is little danger of all the nitrogen becoming available too quickly before it can be utilized by the crop. In the case of paddy soils, however, the conversion of the cyanamide nitrogen into ammoniacal nitrogen is very rapid, and we are not yet in a position to say how this affects the assimilation of the ammoniacal nitrogen by the paddy plant. Ammonia being fixed by the soil, there is little likelihood of loss taking place in this case, whereas if nitrates in garden soil were produced at an equal rate, loss would undoubtedly occur.

DICYANODIAMIDE AND ITS INFLUENCE ON PLANT GROWTH.

There has been a great deal of discussion in chemical literature concerning dicyanodiamide, and the views expressed by various investigators are of a conflicting nature both in regard to its formation in the soil and to its properties. Much of the data available is not entitled to serious consideration from an agricultural point of view owing to the fact that excessive quantities of nitrogen were used which would never be employed in practice. Moreover,

the method of analysis employed in some of the previous experiments are open to serious objection in that the precipitants used were not specific for dicyanodiamide. The problem is under thorough investigation by us and the preliminary results so far obtained may be discussed here.

In dosages ordinarily used in agricultural practice we have not been able to detect the presence of dicyanodiamide at any stage of the decomposition of calcium cyanamide. But when the dosage is considerably increased, dicyanodiamide is formed, the further decomposition of which seems to be very slow. For instance, when cyanamide nitrogen was applied to the soil at the rate of 83 milligrammes and 166 milligrammes per 100 grammes of soil, 11·5 milligrammes and 60 milligrammes respectively were found after 14 days and 4½ months respectively.

Form and rate of N applied per 100 grammes soil	Analysis carried out after	Milligrammes of dicyanodiamide found
	Days	
10 milligrammes cyanamide N	1	0·0 or 0 per cent.
83 Do. do.	14	11·5 or 25 ,,
166 Do. do.	135	60·0 or 36 ,,
13 milligrammes of pure dicyanodiamide N ..	2	10·0 or 77 ,,
20 Do. do.	135	1·0 or 5 ,,

While it is admitted that the evidence before us is insufficient to make a definite statement in regard to the formation of dicyanodiamide during the decomposition of cyanamide in the soil, we may form some conclusions having regard to the conditions that are known to favour its production.

We see from the statement above that dicyanodiamide, whether formed from cyanamide or added in the pure state, persists as such in the soil for some time, and as we have not been able to detect it at any stage of the decomposition when cyanamide is added in ordinary agricultural doses, it is probable that

under such conditions no dicyanodiamide is formed. The fact that dicyanodiamide is formed when high concentrations of nitrolim are employed shows that there is a limit of safety in the use of this fertilizer.

Moreover, it indicates the necessity for thorough incorporation of the manure in the soil when applied, otherwise local areas of high concentration may easily be formed leading to the production of dicyanodiamide. This, perhaps, explains why manuring with cyanamide even in ordinary dosages is sometimes reported to be harmful.

We may also form some idea as to why under these conditions dicyanodiamide should form in the soil. Cyanamide in an acid or alkaline medium polymerises into dicyanodiamide. When calcium cyanamide is added to the soil, in contact with the soil moisture it resolves into cyanamide and calcium hydroxide. If the dosage be small and the manure thoroughly incorporated into the soil, no dicyanodiamide is formed. If, on the other hand, the dosage is large or the manure is not thoroughly and uniformly mixed with the soil, a relatively high percentage of calcium hydroxide will be formed in those areas where the manure happens to be concentrated. It is quite likely that this local concentration of alkali may be sufficient to bring about polymerisation of the cyanamide into dicyanodiamide. The hydrolysis of the calcium cyanamide and the amount of free calcium hydroxide present in the soil seem to be the factors determining the formation of dicyanodiamide. This view is based only on theoretical considerations and needs, of course, to be confirmed by further observations. As regards the fate of dicyanodiamide formed in, or added to, the soil, we have seen that it does not remain as such permanently but slowly changes into some other compounds, the chemical nature of which we are not yet in a position to explain. Experiments to induce the rapid disappearance of dicyanodiamide from the soil show signs of promise. More than this cannot at present be said.

Toxic influence of dicyanodiamide.

Dicyanodiamide even in such large doses as 5 cwt. per acre has not affected germination in our trials with sixteen varieties of cereals and pulses commonly cultivated in South India. A few days after germination, however, all the plants showed signs of nitrogen starvation. When nitrogen, however, was applied in the form of potassium nitrate, the plants began to grow again normally. Our results agree in this respect entirely with those of Cowie in regard to the influence of dicyanodiamide on germination and growth.

Table XII.

Showing the effect of dicyanodiamide on germination and growth of plants.

(The salt was applied in the form of a solution of pure dicyanodiamide to small quantities of soil in pots at rates representing 1 cwt., 3 cwt. and 5 cwt. per acre.)

S. No.	Local or popular name	Botanical name	Control	Dicyanodiamide	
				Germination	Growth 15 days after sowing
				1, 3 & 5 cwt.	1, 3 & 5 cwt.
1	Wheat ..	*Triticum* sp. ..	All germinated well and growing well after a fortnight.	All germinated and growing well.	All showing signs of nitrogen starvation. *Ragi* seems to be most affected. The addition of potassium nitrate to the soil revived the plants and growth was again normal.
2	Gingelly ..	*Sesamum indicum* ..			
3	Paddy ..	*Oryza sativa* ..			
4	Cholam ..	*Sorghum vulgare* ..			
5	Red-gram ..	*Cajanus indicus* ..			
6	Horse-gram ..	*Dolichos biflorus* ..			
7	Ragi ..	*Eleusine coracana* ..			
8	Bengal-gram	*Cicer arietinum* ..			
9	Black-gram ..	*Phaseolus mungo* ..			
10	Samai ..	*Panicum miliare* ..			
11	Cow pea ..	*Vigna catjang* ..			
12	Cumbu ..	*Pennisetum typhoideum*			
13	Tenai ..	*Setaria italica* ..			
14	Kudurai vali	*Panicum crus-galli* ..			
15	Panivaragu ..	*Panicum miliaceum* ..			
16	Lab lab ..	*Dolichos lablab* ..			

A soil, to which dicyanodiamide was added at the rate of 5 cwt. per acre, grew ragi (*Eleusine coracana*) splendidly after six months. The photographic reproductions are given in Plate I, fig. 4. The dicyanodiamide in this period has therefore been converted into harmless products.

We have just now seen that the adverse influence of dicyanodiamide on the crop is to prevent the supply of nitrogen to it. This means that the process of

nitrification is inhibited or retarded. The results of experiments to check this are embodied in Table XIII and graphically represented in Chart II.

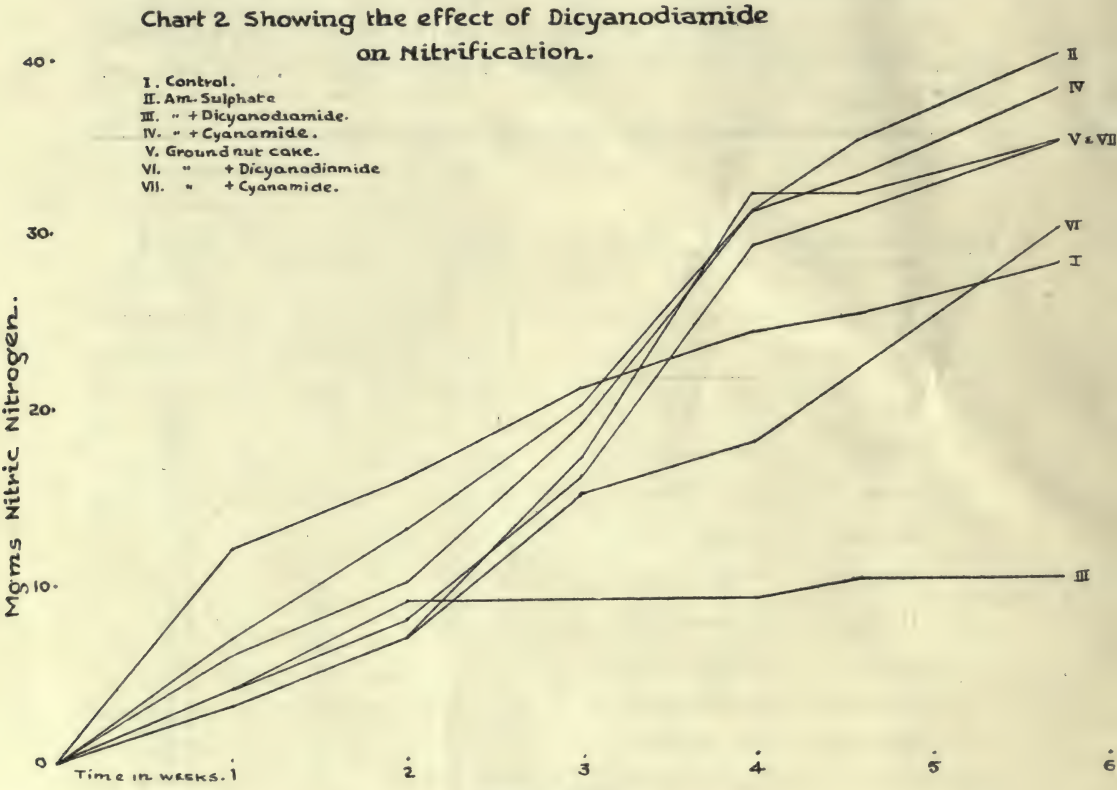

TABLE XIII.

Showing the influence of dicyanodiamide on nitrification.

(50 milligrammes of nitrifiable N per kilo of soil.
25 milligrammes of dicyanodiamide N per kilo of soil.)

Nature of treatment	MILLIGRAMME OF NITRATE N FOUND AFTER DAYS					
	7	14	21	28	32	40
Control	12·0	16·0	21·0	24·0	25·0	28·0
Ammonium sulphate	7·0	13·0	20·0	31·0	35·0	40·0
Ammonium sulphate and dicyanodiamide	4·0	9·0	9·0	8·8	10·0	9·8
Ammonium sulphate and cyanamide	6·0	10·0	19·0	31·0	33·0	38·0
Groundnut cake	3·0	7·0	17·0	32·0	32·0	35·0
Groundnut cake and dicyanodiamide.	2·8	6·9	15·0	18·0	22·0	30·0
Groundnut cake and cyanamide ..	4·0	8·0	15·7	29·0	31·0	35·0

It will be seen that our results again generally confirm Cowie's observations. In our experiments the rate of nitrification, where this occurred, was, as would be expected, more rapid than in Cowie's experiments. One very interesting fact to be noted is that dicyanodiamide does not seem to affect the nitrification of groundnut cake so drastically as that of ammonium sulphate. Cowie also had a similar experience in the nitrification of dried blood.

There would appear to be some evidence that in the presence of decomposing organic matter the dicyanodiamide either undergoes change itself or at any rate its toxicity towards the nitrifying organisms is very largely reduced.

Support for this hypothesis is found in the observation we have made that dicyanodiamide when added to cattle dung rapidly disappears though there is practically no change if the urine alone is used.

If confirmed, this observation may lead to results of considerable practical importance in the use of nitrolim as a fertilizer.

Summary.

1. Calcium cyanamide when applied to the soil in ordinary agricultural doses is not harmful to crops.

2. No lapse of time between the application of the manure and sowing is necessary.

3. Calcium cyanamide rapidly decomposes in the soil into urea, this change being chemical or physico-chemical in nature; the hydrolysis of urea to ammonia and its subsequent oxidation to nitrates is a biochemical process.

4. Dicyanodiamide is not produced in the soil from calcium cyanamide when it is applied in normal doses and thoroughly incorporated in the soil, but may be produced when high concentrations of nitrolim are employed.

5. Dicyanodiamide decomposes in the soil with considerable slowness.

6. Dicyanodiamide does not affect germination, but inhibits nitrification. This inhibition is more pronounced in the case of ammonium sulphate than in the case of organic nitrogenous substances such as groundnut cake.

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